

The University of Chicago

THE SOLUBILITY OF ARAGONITE IN SALT SOLUTIONS

A PART OF A DISSERTATION SUBMITTED TO
THE FACULTY OF THE DIVISION OF THE
BIOLOGICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY
AND PHARMACOLOGY

1935

By
AUDRA ARNOLD BROWMAN

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Aragonite, the rhombic form of calcium carbonate, is found in the hard parts of many invertebrates and in the otoliths of some fish and amphibians. Recently it has also been found in human biliary calculi (1). It is surprising that aragonite is present in animal life, because it is usually metastable below 90°, and where solid CaCO_3 is found, one would expect it to be calcite, the stable form of calcium carbonate. Calcite, the hexagonal form of calcium carbonate, is frequently found in invertebrates. The study of why aragonite is found in some invertebrates and calcite in others, and why aragonite should be formed at all in animal life necessarily involves the question of its solubility. Bäckström (2) made a careful study of the solubility of aragonite and calcite at 9°, 25°, and 35°, at ionic strengths varying between 0.044 and 0.026. Since, however, no determinations seem to have been made at 38°, or at an ionic strength as great as that of serum, the present work was undertaken.

Theoretical

At equilibrium, and in conformity with previous usage, $[\text{Ca}^{++}] \times [\text{CO}_3^{--}] = K'_{sp}$, where K'_{sp} is the stoichiometric solubility product. In logarithmic form this equation becomes

$$-\log [\text{Ca}^{++}] - \log [\text{CO}_3^{--}] = -\log K'_{sp} = \text{p}K'_{sp}$$

It is the purpose of the present paper to present the results of the determination of $\text{p}K'_{sp}$ of aragonite as a function of ionic strength.

The $[\text{CO}_3^{--}]$ was calculated from the equation of Hastings, Murray, and Sendroy (3)

$$[\text{CO}_3]^- = \frac{[\text{total CO}_2] \times K'_1 \times K'_2}{[\text{H}^+]^2 + [\text{H}^+] \times K'_1 + K'_1 K'_2}$$

where K'_1 and K'_2 are the apparent first and second dissociation constants of carbonic acid respectively. K'_1 and K'_2 vary with the ionic strength according to the equations of Hastings and Sendroy (4), $\text{p}K'_1 = 6.33 - 0.5 \sqrt{\mu}$ and $\text{p}K'_2 = 10.22 - 1.1 \sqrt{\mu}$.

EXPERIMENTAL

Salt solutions, varying in ionic strength from 0.012 to 0.230 were equilibrated at 38° with aragonite for 20 to 40 hours. CO_2 was present in the gas phase in an amount such that the pH at equilibrium varied between 7.2 and 7.6. At the end of the equilibration period, the solutions were centrifuged and the supernatant fluid removed for analysis without exposure to air. The fluid was analyzed for its pH, CO_2 , and Ca. From these data the $[\text{CO}_3^-]$ and the product $[\text{CO}_3^-] \times [\text{Ca}^{++}]$ were calculated.

Before the experiments on the solubility of aragonite were carried out, a series of determinations of the solubility of calcite at ionic strengths varying from 0.011 to 0.228 was carried out and found to agree with those previously found by Hastings, Murray, and Sendroy (3).

pH—The pH was determined colorimetrically by having phenol red present in the solution in a concentration of 0.00075 per cent and matching the color with bicolor standards made according to the procedure of Hastings and Sendroy (5). This could be done within ± 0.01 pH. Since the ionic strength of the solution varied, it was necessary to take into account the change in the apparent dissociation constant of the indicator with ionic strength. This was done by using the appropriate constant for the particular ionic strength as determined by Sendroy and Hastings (6). The bicolor standards were checked against phosphate standards, which had been electrometrically standardized.

CO₂—The CO_2 was determined by the method of Van Slyke and Neill (7), with the manometric gas apparatus.

Calcium—Calcium was determined according to the Clark and Collip (8) modification of the Kramer and Tisdall method.

Analyses were made in duplicate or triplicate.

TABLE I

Solubility of Aragonite At 38° in Solutions of Varying Strength

The initial composition of the solution was as follows: in Experiments 1 to 3 $\text{NaHCO}_3 = 10$ mm per liter; in all other experiments $\text{NaHCO}_3 = 25$ mm per liter. NaCl was present as stated. 40 cc. of solution were equilibrated with 0.5 gm. of aragonite.

Experiment No.	NaCl	μ	$\sqrt{\mu}$	pH	[CO ₂]	[CO ₃ =]	[Ca ⁺⁺]	pK' _{sp} CaCO ₃	
								Determined	Calculated*
	<i>M per l. × 10³</i>				<i>M per l. × 10³</i>	<i>M per l. × 10³</i>	<i>M per l. × 10³</i>		
1		0.012	0.109	7.50	13.25	0.0313	0.28	8.06	8.00
2		0.012	0.109	7.485	13.06	0.0296	0.33	8.01	8.00
3		0.012	0.109	7.58	12.92	0.0371	0.30	7.95	8.00
4		0.027	0.164	7.515	29.22	0.0821	0.19	7.81	7.82
5		0.027	0.164	7.47	30.53	0.0775	0.17	7.88	7.82
6	10	0.037	0.193	7.51	30.32	0.0907	0.18	7.79	7.74
7	20	0.047	0.218	7.47	30.15	0.0880	0.24	7.68	7.66
8	20	0.047	0.218	7.475	30.68	0.0905	0.24	7.66	7.66
9	20	0.048	0.218	7.505	30.48	0.0969	0.26	7.60	7.66
10	30	0.058	0.240	7.39	30.88	0.0778	0.31	7.62	7.61
11	40	0.067	0.260	7.455	30.13	0.0958	0.24	7.63	7.56
12	40	0.068	0.261	7.49	31.26	0.1078	0.25	7.58	7.56
13	40	0.067	0.260	7.425	29.52	0.0868	0.29	7.60	7.56
14	50	0.078	0.280	7.215	31.96	0.0588	0.57	7.47	7.51
15	70	0.098	0.312	7.495	30.04	0.1205	0.23	7.56	7.44
16	70	0.098	0.312	7.335	30.40	0.0806	0.34	7.56	7.44
17	70	0.098	0.312	7.305	30.78	0.0754	0.57	7.37	7.44
18	80	0.108	0.330	7.245	31.92	0.0715	0.57	7.39	7.40
19	90	0.118	0.344	7.365	31.24	0.0984	0.43	7.37	7.36
20	90	0.118	0.344	7.245	31.34	0.0736	0.67	7.31	7.36
21	100	0.128	0.358	7.505	30.57	0.1415	0.32	7.35	7.32
22	100	0.128	0.358	7.235	31.20	0.0749	0.68	7.30	7.32
23	110	0.138	0.372	7.345	31.18	0.1001	0.49	7.31	7.31
24	120	0.148	0.384	7.39	30.40	0.1113	0.43	7.32	7.28
25	120	0.148	0.384	7.355	30.97	0.1040	0.46	7.32	7.28
26	130	0.158	0.397	7.405	30.40	0.1184	0.41	7.32	7.25
27	130	0.159	0.399	7.225	31.50	0.0790	0.76	7.21	7.25
28	140	0.168	0.410	7.34	30.89	0.1075	0.55	7.23	7.23
29	140	0.169	0.411	7.285	30.46	0.0920	0.70	7.19	7.23
30	150	0.179	0.423	7.31	31.34	0.1031	0.71	7.14	7.21
31	160	0.189	0.434	7.26	31.40	0.0964	0.67	7.19	7.19
32	160	0.189	0.434	7.435	30.98	0.1456	0.48	7.16	7.19

* Calculated $\text{pK}'_{\text{sp}}\text{CaCO}_3$ derived from $\text{pK}'_{\text{sp}}\text{CaCO}_3 = 8.42 - \frac{4.48 \sqrt{\mu}}{1 + 1.34 \sqrt{\mu}}$.

TABLE I—*Concluded*

Experi- ment No.	NaCl	μ	$\sqrt{\mu}$	pH	[CO ₂]	[CO ₃ ⁼]	[Ca ⁺⁺]	pK' _{sp} CaCO ₃	
								Deter- mined	Calcu- lated*
	<i>M</i> per l. × 10 ³				<i>M</i> per l. × 10 ³	<i>M</i> per l. × 10 ³	<i>M</i> per l. × 10 ³		
33	170	0.199	0.446	7.28	31.50	0.1033	0.68	7.15	7.17
34	180	0.209	0.456	7.32	31.52	0.1169	0.60	7.15	7.15
35	180	0.209	0.456	7.30	31.72	0.1120	0.69	7.11	7.15
36	190	0.219	0.467	7.255	31.38	0.1026	0.84	7.06	7.14
37	200	0.228	0.477	7.335	30.80	0.1272	0.60	7.12	7.12
38	200	0.228	0.478	7.425	31.04	0.1605	0.44	7.15	7.12
39	200	0.229	0.478	7.315	31.12	0.1220	0.81	7.00	7.12
40	200	0.230	0.480	7.245	34.30	0.1146	0.86	7.01	7.12

Results

The analytical results and the values of pK'_{sp} calculated therefrom are given in Table I. The values of pK'_{sp} have been plotted against $\sqrt{\mu}$ in Fig. 1. The equation of the upper line, obtained as previously described (3), is

$$\text{pK}'_{sp} = 8.42 - \frac{4.48 \sqrt{\mu}}{1 + 1.34 \sqrt{\mu}}$$

where 8.42 is the pK of aragonite at zero ionic strength.

A comparison between the values of pK' calculated from this equation and those found by experiment is given in the last two columns of Table I.

The lower line on Fig. 1 is the curve of the solubility product of calcite as a function of ionic strength. It will be seen that the pK'_{sp} of aragonite is 0.15 less than that of calcite, although the change in solubility with change in ionic strength is the same. This means that aragonite is more soluble than calcite at the same ionic strength, the ratio of the constants being $K_{\text{aragonite}}/K_{\text{calcite}} = 1.41$. When the constants are corrected to the same terms as those calculated by Bäckström (2), the agreement is satisfactory between our results and his at the same ionic strength and at the same temperature. The value of pK'_{aragonite} at the ionic strength of body fluids is 7.25, whereas that of pK'_{calcite} is 7.40.

Through the kindness of Dr. Dallas B. Phemister, we were able to determine the solubility of two gallstones which by chemical analysis consisted largely of calcium carbonate, and which, according to their x-ray spectrograms, consisted of aragonite. The pK'_{sp} values of these gallstones were respectively 7.28 and 7.34. At this ionic strength, the pK' of aragonite is 7.27, whereas that of calcite is 7.42. There is thus afforded independent evidence that

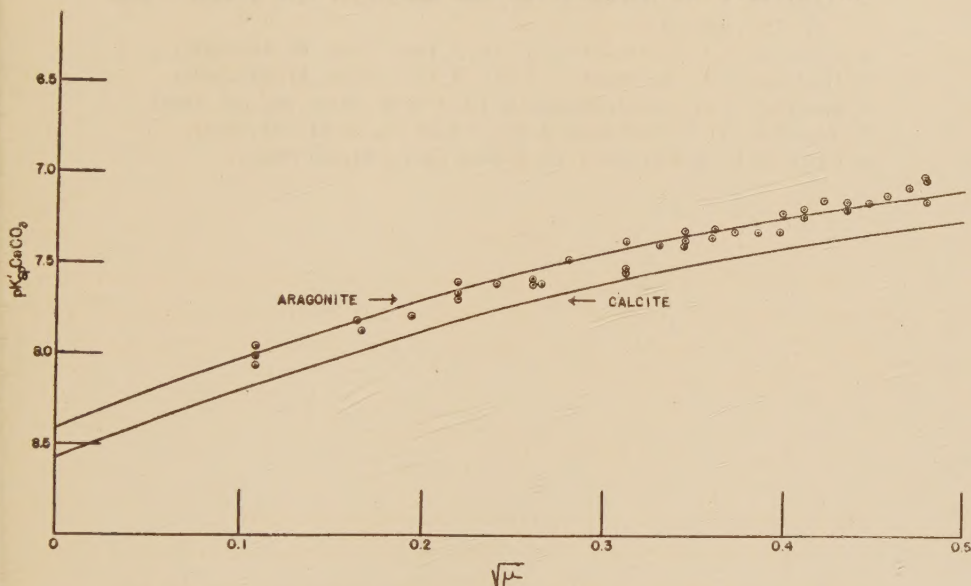


FIG. 1. The solubility of $CaCO_3$ in salt solutions of varying ionic strength saturated with $CaCO_3$ at 38° . Values of $pK'_{sp}CaCO_3$ are plotted as ordinates and $\sqrt{\mu}$ as abscissæ. The lower curve represents calcite and the upper curve represents aragonite. The aragonite curve has the equation

$$pK'_{sp}CaCO_3 = 8.42 - \frac{4.48\sqrt{\mu}}{1 + 1.34\sqrt{\mu}}$$

the calcium carbonate of these gallstones belonged to the rhombic form aragonite.

SUMMARY

The solubility of aragonite has been studied as a function of ionic strength and compared with that of calcite.

Aragonite is more soluble than calcite, the ratio of their solubility products being 1.41.

The solubility product of calcium carbonate gallstones has been found to correspond to that of aragonite.

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